TITLE: DEVELOPMENT OF ACTIVATED CARBONS FROM COAL COMBUSTION BY-PRODUCTS

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1. ABSTRACT

Program Introduction: Rationale, Objective and Research Design

Due to more stringent environmental regulations, especially concerning NOx emissions, there is an alarming rise in carbonaceous waste in fly ash, unburned carbon, from coal combustion processes. However, the fate of these products is mainly disposal, due to the present lack of routes for their effective use. Nevertheless, the unburned carbon is a highly attractive raw material for the production of activated carbons, since it has gone through a devolatilization process while in the combustor, and therefore, only requires to be activated. Accordingly, the overall objective of this research is to develop adsorbent materials from coal combustion by-products (CCBPs). In this research program, the following three tasks have been defined:

- Samples from different combustion processes are collected, including pulverized, cyclone, stoker firing and fluidized-bed combustion, to secure that the findings can be applied to the

different combustion technologies used by the power industry. The properties of this unique suite of CCBPs are extensively characterized by a wide range of analytical techniques.

- Several routes for the preparation of activated carbons are proposed to be investigated, including physical activation with different gases, such as steam and CO_2, at various flowrates and temperatures, as well as chemical activation.

- The properties of the resultant activated carbons are systematically characterized, especially their porous structure. This will provide information for the understanding of the mechanisms involved in the generation of activated carbon from unburned carbon and also to establish the optimum route for the production of activated materials.

Upon completion of this research program, a novel cost-effective process for the production of adsorbent materials from CCBPs will have been extensively investigated. This will have a double environmental and economical impact, since CCBPs that are currently being disposed, can be used as precursors for the production of premium carbon products like activated carbons.

Accomplishments Achieved During the Current Period of Performance

During the current period of performance, July 1999 – April 2000, the following tasks have been conducted, as scheduled in the project proposal:

1. Procurement and characterization of the suite of CCBPs.
   The samples collected have been produced in a variety of combustion processes, including: (i) pulverized utility boilers, where two samples were collected from systems retrofitted with low- NOx burners (243 and 180 MW, respectively) and one from an unit that has been retrofitted with a Selective Non Catalytic Reduction system (136 MW); and (ii) one sample collected from an utility cyclone unit (216 MW).
   A series of analysis were conducted on the above samples to characterize their physical and chemical properties. The tests conducted thus far include:
   (i) Determination of the loss-on-ignition (LOI) contents according to the ASTM C311 procedure, where for fly ashes commonly derived from Eastern U.S. coals, the LOI value essentially equates to carbon content. As expected, the sample from the cyclone unit contained the highest carbon content (LOI of ~ 80%), since this unit has been retrofitted with a technology to separate the unburned carbon form the fly ash. In contrast, the sample from the unit retrofitted with a Selective Non Catalytic Reduction system showed the lowest carbon content with LOI values around 2-4%. The samples from the utility boilers with low-NOx burners were collected from the hot-side hoppers and present carbon contents ~ 50%.
   (ii) Characterization of their inherent porosity by conducting N_2 adsorption isotherms at 77K using a Quantachrome adsorption apparatus. The BET (N_2 77K) surface areas of the samples investigated were between 30-40 m^2/g. Pore size distribution studies were also conducted and showed that the pore volume is mainly due to mesopores, with the mesopore volume accounting for over 60% of the

total pore volume, where the extensive and rapid devolatilization that coal undergoes in the combustor, seems to promote the generation of meso- and macropores.

2. Development and characterization of activated carbons from CCBPs.
   The activation of the unburned carbon samples has also been initiated during this period. These experiments were carried out in an activation furnace, that consists of a stainless steel tube reactor inside a vertical tube furnace. The samples were physically activated using steam and CO_2 at 850°C. The preliminary experiments conducted indicate that the samples activated with steam present generally higher surface areas than those using CO_2 for the same period of time, probably due to the faster reaction rate of steam. Surface areas as high as 450 m^2/g were achieved for unburned carbon samples activated with steam.

Plans for the Coming Year

The work planned for the coming year include the following tasks:

- Finalize the procurement of the suite of CCBPs. It is anticipated that this will include samples from a suspension-fired research boiler (2 MM Btu/hour) operated by The Energy Institute, a stoker and a fluidized bed.
- Design a battery of tests to characterize the samples assembled. It is anticipated that these tests will include the above LOI and surface area measurements as well as optical microscopy studies.
- Continue the activation of the unburned carbon samples under a wider range of controlled operating variables in order to establish the optimum route for the generation of activated carbon materials.
- Publish widely the outcome of these investigations.

2. LIST OF PUBLISHED JOURNAL ARTICLES, COMPLETED PRESENTATIONS AND STUDENTS RECEIVING SUPPORT FROM THE GRANT

Conference presentations

- Development of Activated Carbons from Coal Combustion By-Products, M. Mercedes Maroto-Valer, Zhe Lu, and Harold H. Schobert, 17th Annual International Pittsburgh Coal Conference, 2000, Submitted.

Students Supported under this Grant

- Zhe Lu, graduate student in the Department of Energy and Geo-Environmental Engineering, The Pennsylvania State University